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Influence of vapors of volatile organic compounds on spectral shift of bending vibrations of freely suspended ferroelectric liquid-crystal films

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The influence of the vapors of volatile inert fluorocarbon compounds on the mechanical properties of freely suspended ferroelectric liquid-crystal films has been studied. It was shown that spectral shift of bending vibrations of freely suspended films depends on the mass variations of the associated ambient gas as well as on the adsorption of the vapors of volatile fluorocarbon compounds onto the film surface. It was also shown that adsorption layers similar to surfactants decrease the film surface tension by 11%–35% (4–12.5 dyn/cm). © 2004 American Institute of Physics. [DOI: 10.1063/1.1697630]

Because of the absence of confined surfaces, freely suspended liquid-crystal films have been, since 1922,¹ canonical objects for x-ray studies of the structure of smectic mesophases, and from the end of the 1970's, they have been used for fundamental studies of the properties of two-dimensional (2D) systems.^{2–4} At present, a number of works devoted to the practical implementation of freely suspended films as pressure,⁵ IR, and visible (Golay cell)⁶ detectors and parametric converters⁷ have been published.

In this letter, we report on a method of studying the adsorption of volatile organic compounds onto the surface of freely suspended films by the linear electromechanical effect.^{8–11} It should be noted that this study was strongly motivated by the results presented in Ref. 12 where a similarity between surfactants and layers of fluorocarbon compounds adsorbed on the surface of several organic solvents was observed.

The basic property of a freely suspended liquid-crystal film surface is its reduction to the minimal surface.¹³ In the simple case of the flat minimal surface spanned on a rectangular contour, and neglecting the edge effect (meniscus), the equation of a motion of freely suspended film is a 2D wave equation. Considering the flat minimal surface as a rectangular membrane, its eigenfrequencies are dependent on the parameters of the film material as follows:¹³

$$\nu_{nm} = \frac{1}{2} \sqrt{\frac{2\sigma}{\rho_s} \left(\frac{n^2}{a^2} + \frac{m^2}{b^2} \right)}, \quad (1)$$

where a and b are, respectively, the length and the width of the film, σ is the surface tension, $\rho_s = N\ell\rho_{LC} + H\rho_{air}$ is the two-dimensional mass density, N stands for the number of smectic layers, ℓ is the interlayer distance, H is the thickness of air moving with the film, and ρ_{LC} and ρ_{air} are the bulk densities of liquid crystal and air. The integers n and m denote the normal modes. In practice, the discrete spectrum of pure tones is transformed to a set of separated spectral reso-

nant bands of finite width, the positions of which are extremely sensitive to changes in both the parameters of the film and the pressure of ambient gas.

Under this approximation, the value of surface tension and the 2D density of a liquid, such as smectic A and the more ordered smectic B liquid crystals, might be calculated from the spectrum of mechanical vibrations.¹⁴ From Eq. (1), it follows that the eigenfrequency changes of the film depend on mass variations of the associated ambient gas as well as on the surface tension of the film. In the general case, these changes can be independent, i.e.,

$$\frac{f'_1}{f_2} = \sqrt{\frac{\sigma_1}{\sigma_2}}, \quad \text{and} \quad \frac{f_1}{f'_1} = \sqrt{\frac{\rho_{s2}}{\rho_{s1}}}, \quad (2)$$

where f_1 is the eigenfrequency of the film with parameters ρ_{s1} , σ_1 , and f_2 is the eigenfrequency of the film with changed parameters ρ_{s2} and σ_2 for the same mode (same n and m). From Eq. (2), it follows that the frequency shift $f_1 - f'_1$ is defined by a 2D mass density variation, whereas the frequency shift $f'_1 - f_2$ is defined by the tension variation of the surface.

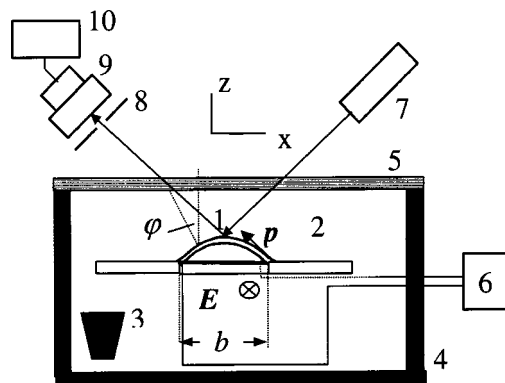


FIG. 1. Setup for the study of the influence of the vapors of volatile organic compounds on spectral shift of bending vibrations of freely suspended liquid-crystal films: (1) Ferroelectric freely suspended liquid-crystal film, (2) glass plate with rectangular $2 \times 10 \text{ mm}^2$ hole and two conductive Al electrodes, (3) vessel with volatile liquid, (4) hermetically sealed chamber, (5) glass plate, (6) sound generator with amplifier, (7) He–Ne laser, (8) iris diaphragm, (9) Si photodiode, and (10) Fourier spectrometer.

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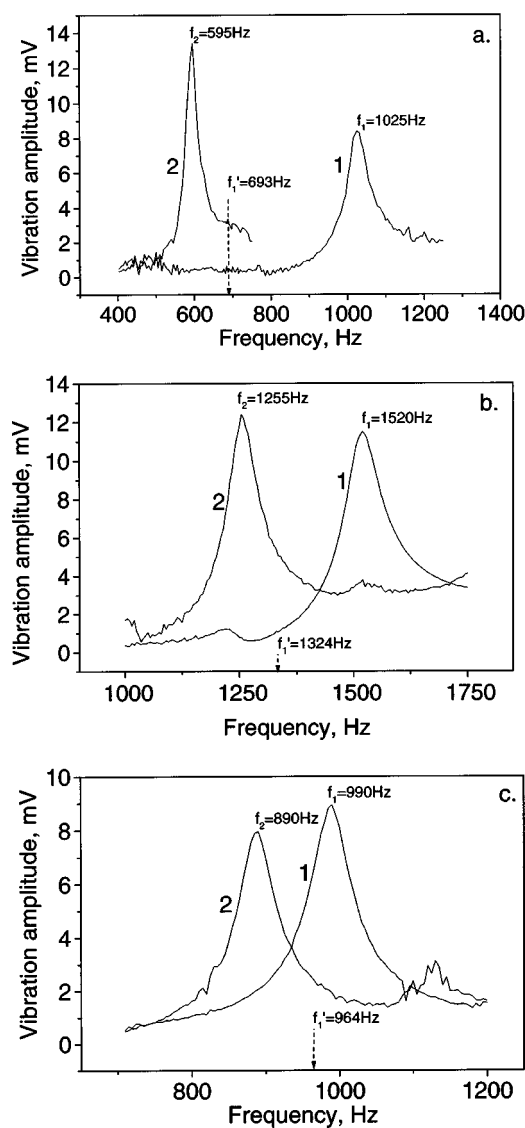


FIG. 2. (a)–(c) Resonance band shifts of low-frequency bending vibrations of the freely suspended ferroelectric films (CS-1029, $2 \times 10 \text{ mm}^2$) in pure atmospheric air (curves 1) and in the presence of volatile organic compounds (curves 2). (a) Compound C_6F_{14} (molecular mass $M = 338$, partial pressure $p = 102 \text{ Torr}$, $f_1 = 1025 \text{ Hz}$, $f_1' = 693 \text{ Hz}$, $f_2 = 595 \text{ Hz}$, film surface tension decrease caused by vapor adsorption onto the film surface $\Delta\sigma = 12.5 \text{ dyn/cm}$, and number of layers $N = 157$). (b) Compound C_8F_{18} ($M = 438$, $p = 20 \text{ Torr}$, $f_1 = 1520 \text{ Hz}$, $f_1' = 1324 \text{ Hz}$, $f_2 = 1255 \text{ Hz}$, $\Delta\sigma = 4 \text{ dyn/cm}$, and $N = 157$). (c) Compound C_9F_{20} ($M = 488$, $p = 6.5 \text{ Torr}$, $f_1 = 990 \text{ Hz}$, $f_1' = 964 \text{ Hz}$, $f_2 = 890 \text{ Hz}$, $\Delta\sigma = 6.12 \text{ dyn/cm}$, and $N = 195$). All measurements were carried out under normal ambient conditions ($p = 10^5 \text{ Pa}$, $T = 20^\circ\text{C}$). Bending vibrations were excited by sinusoidal voltage of constant amplitude $U = 30 \text{ V}$ and variable frequency. Vibration amplitude of $0.8 \text{ }\mu\text{m}$ corresponds to photovoltage of 10 mV .

The vibrations of the film can be excited acoustically or, as in this work, by applying an electric field E parallel to the surface of the film, which interacts with the surface spontaneous polarization p as shown in Fig. 1. At present, there is no consistent theory which describes the vibration excitation of the ferroelectric membrane in the direction perpendicular to the lateral electric field, although it is clear that an adequate theoretical model should take into consideration the spatial heterogeneity of spontaneous polarization of the membrane that is deformed when moving, and the backflow in the liquid crystal.^{5,15,16}

Our experiments were conducted on films of room-

TABLE I. Parameters of the films and organic liquids.

Compounds	N (number of smectic layers)	Molecular mass	Partial pressure (Torr)
C_6F_{14}	195	338	102
C_8F_{18}	157	438	20
C_9F_{20}	157	488	6.5
C_6H_{14}	185	86	120

temperature ferroelectric SmC^* mixture CS-1029 from Chisso [Cr (-18°C), SmC^* (73°C), SmA (85°C), and N^* (95°C) iso.]. The preparation process of freely suspended films has been described elsewhere.¹⁷ The films were drawn across a rectangular hole made in a glass slide of 2 mm thickness. The film holders were contained on a heating stage, and the film can be stabilized at a given temperature to $\pm 0.1^\circ\text{C}$. The film thickness was measured by means of reflection spectroscopy using the photomultichannel analyzer. For the excitation of the vibration modes, alternating voltage was applied across the electrodes. In the setup shown in Fig. 1, the laser beam reflected from the surface of the film was detected by a split photodiode that was used as a position-sensitive detector. The optical response, proportional to the z displacement of the film, was analyzed using a lock-in amplifier. The deformation of the film was sensitive to the polarity of the applied electric field, therefore the linear electromechanical effect was detected. The amplitude of the second harmonic of the optical response, due to the change of the reflectivity of the film, comprised only an insignificant part of the total signal.

In this work, the influence of the vapors of three fluorocarbon compounds; C_6F_{14} , C_8F_{18} , and C_9F_{20} on the bending vibration spectra of freely suspended ferroelectric liquid-crystal films has been studied. These compounds are the liquid analogs of Teflon; they are absolutely inert and other similar fluorocarbons are used in surgery as components of artificial “blue” blood, since they transfer oxygen and carbon dioxide well (better than erythrocytes).¹²

The film bending vibration spectra were measured in pure atmospheric air and in atmospheric air with saturated vapors of volatile compounds. A small vessel with volatile liquid was placed into the hermetically sealed chamber for 24 h near the freely suspended film to produce saturated vapors.

The main results of the above measurements are represented in Fig. 2. In these diagrams, we can see the resonance shift of all three compounds in the presence of saturated vapors. With the experimental results (Fig. 2) and Eq. (2), we can calculate the resonance shift due to both mass variations of an associated ambient gas and variations of the surface tension. Surface tension of the freely suspended film and the

TABLE II. Experimental data.

Compounds	f_1 (Hz)	f_1' (Hz)	f_2 (Hz)	$f_1 - f_1'$	$f_1' - f_2$	$\Delta\sigma$ (dyn/cm)
				(%)	(%)	
C_6F_{14}	1025	693	595	77.2%	22.8%	12.5 (35.5)
C_8F_{18}	1520	1324	1255	74%	26%	4 (11.3)
C_9F_{20}	990	964	890	26%	74%	6.1 (17.3)

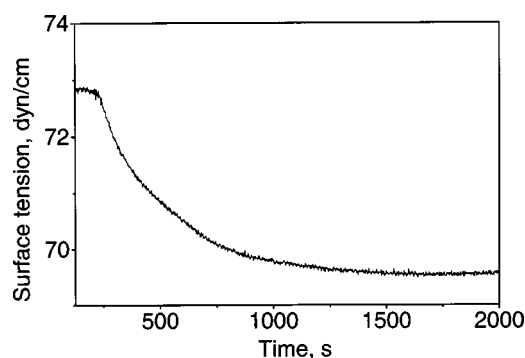


FIG. 3. Water surface tension plotted against hexane (C_6H_{14}) evaporation time. Plateau on the curve corresponds to vapor saturation. Water surface tension decrement caused by vapor adsorption $\Delta\sigma = 3.45$ dyn/cm. All the measurements were carried out under normal ambient conditions ($p = 10^5$ Pa, $T = 20^\circ\text{C}$).

thickness of the associated ambient gas layer H required for the above calculations were obtained in separate experiments as follows: Surface tension of CS-1029 was measured by a classical method described in Ref. 18 and thickness H was obtained by analyses of the frequency shift with known external pressure variations. The following values were obtained: $\sigma_1 = 35.3$ dyn/cm and $H = 3.5$ mm.

The parameters of the films and experimental data obtained from Fig. 2 are shown in Tables I and II.

Analyses of the diagrams in Fig. 2 show that the film bending vibration spectral shifts for the two lower homologues, C_6F_{14} and C_8F_{18} , are mainly due to the mass variations of the associated ambient gas, whereas that for the higher homologue C_9F_{20} is due to surface tension variations connected with vapor adsorption. This behavior roughly correlates with the decrease of partial pressure when the homologue number increases. Vapor adsorption onto the film surface leads to the decrease of surface tension which, for higher homologues (C_8F_{18} and C_9F_{20}), changes by several dyn/cm, which is typical of gas adsorption films.¹⁹ It is known that the surface tension decrease in hydrocarbon films on the water surface is approximately proportional to hydrocarbon partial pressure, which indicates a gaseous state of the adsorption layer, and it obeys the ideal gas equation.¹⁹ For instance, the surface tension decrease of water in the presence of saturated hexane vapor measured by the Langmuir method reached 4 dyn/cm (see Fig. 3), and the films were obviously gaseous. It is noteworthy that in saturated hexane vapors, the electromechanical effect in the freely suspended film is completely absent, which apparently indicates the transition of the ferroelectric liquid crystal to the paraelectric SmA phase.

It was shown in Ref. 19 that the area per admolecule in the gaseous adsorption layer on the water surface is about 100 \AA^2 . By adopting the same value for the case of fluorocarbon vapor adsorption on the liquid-crystal film, we can evaluate the mass of this compound needed to give 3×10^{-12} mole for the film size of $2 \times 10 \text{ mm}^2$. Note that such sensitivity is comparable with that of commercial gas chro-

matography detectors.^{20,21} It is also interesting that, in this case, the freely suspended film simultaneously serves as a gas selector and gas detector.

As far as the homologue C_6F_{14} is concerned, for which the variation in surface tension was 12.5 dyn/cm, the adsorbed film most probably was in a liquid expanded state which is intermediate between gaseous and condensed states.¹⁹

In conclusion, we offer a method of studying vapor adsorption onto the surface of freely suspended liquid-crystal films. A high surface activity of fluorocarbon compounds adsorbed onto the surface of ferroelectric freely suspended liquid-crystal films has been found. The sensitivity of our method appeared to be comparable with that of commercial detectors used in chromatography. We believe that our method can be used in special cases for the detection of volatile liquid vapors undergoing selective adsorption on the chiral liquid-crystal material of freely suspended film.

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